Course Chem 345 Lecturer Gellman

Day Friday Date 3/6/2015

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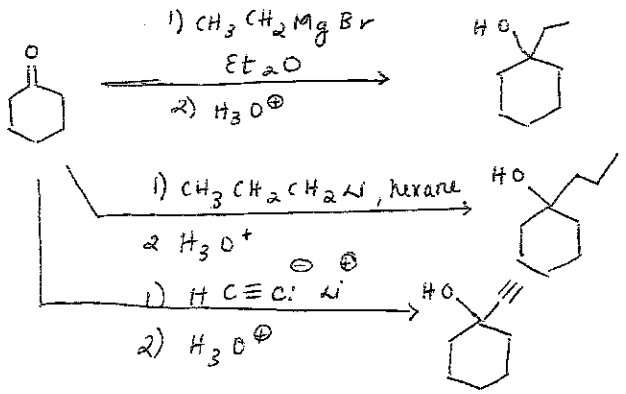
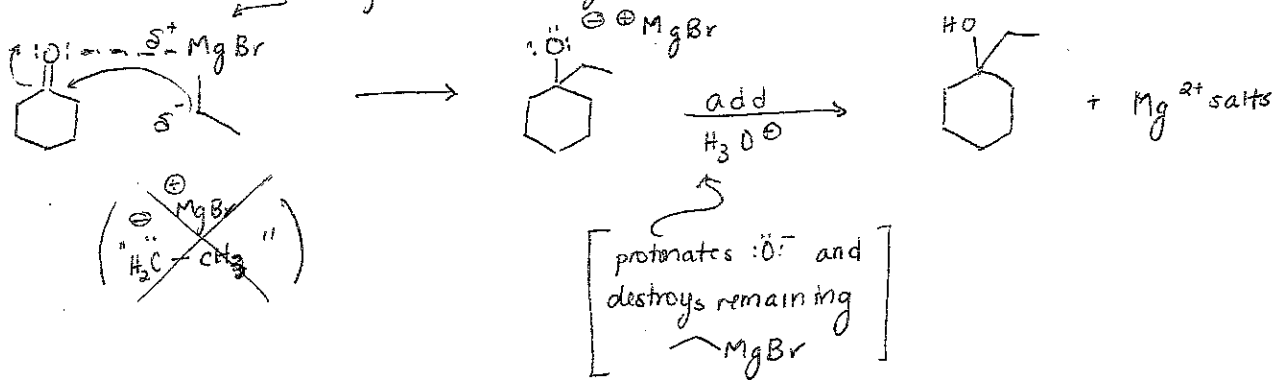
Recall: Rxns of aldehydes/ketones with carbanion reagents....

→ New C-C bonds!

Notes $CH_3CH_2\overset{\delta-}{C}H_2-\overset{\delta+}{Li}$ ("$CH_3CH_2\ddot{C}H_2$ $Li^{\oplus}$")



Mechanism: ← magnesium is acting as a Lewis acid to activate carbonyl



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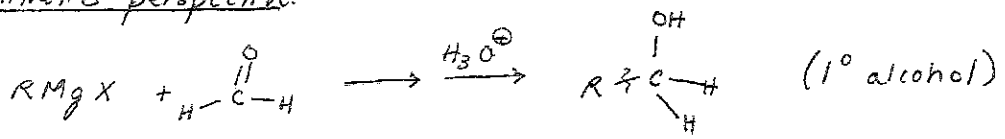
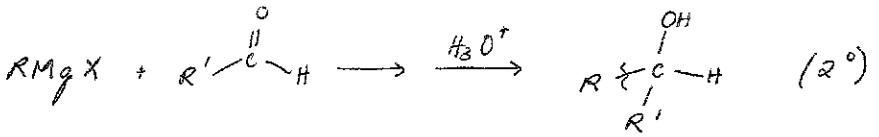
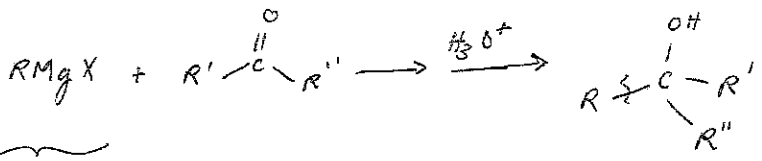
Synthetic perspective:



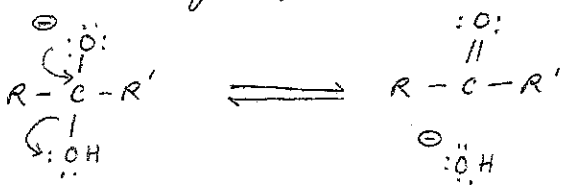




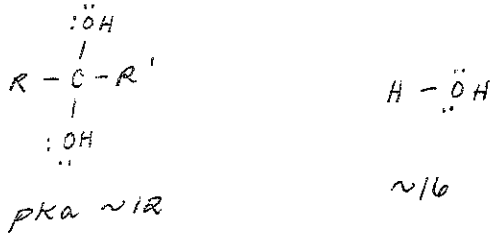
could also use RLi

Reversible vs irreversible addns to C=O.

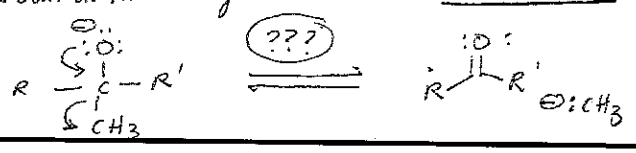
- Reversible: cyanohydrin & hydrate



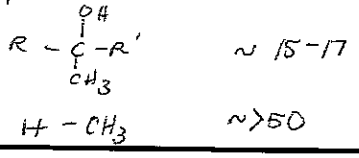
pKa considerations:



- Carbanion like reagent addns are irreversible



pKa considerations:



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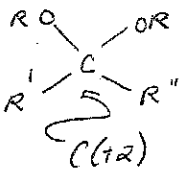
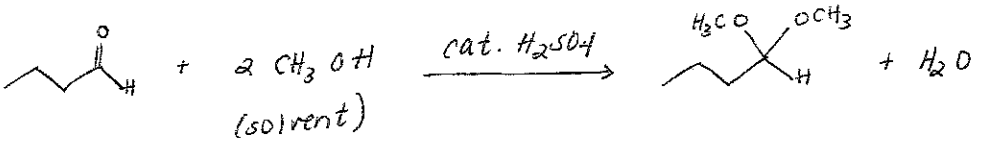
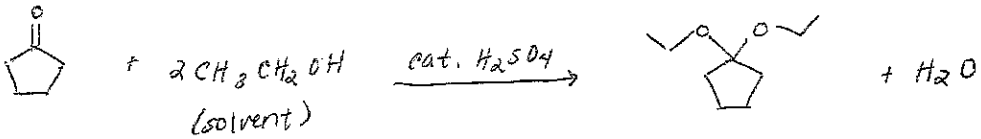
Acetals, formation + use as "protecting groups"

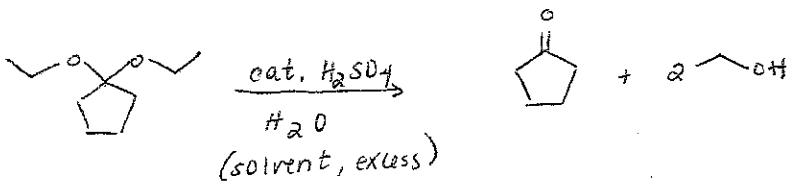
Acetal (generic) –  (a funky kind of ether, w/ special reactivity)

Ex:





* Acetal formation is a reversible process, use principle of mass action (Le Châtliers Principle) to control identity of product
  - For example in rxns above, alcohol is solvent, i.e, present in vast excess, which thermodynamically drives toward acetal.
  - One can "hydrolyze" an acetal to produce the carbonyl cmpd with excess H_2O



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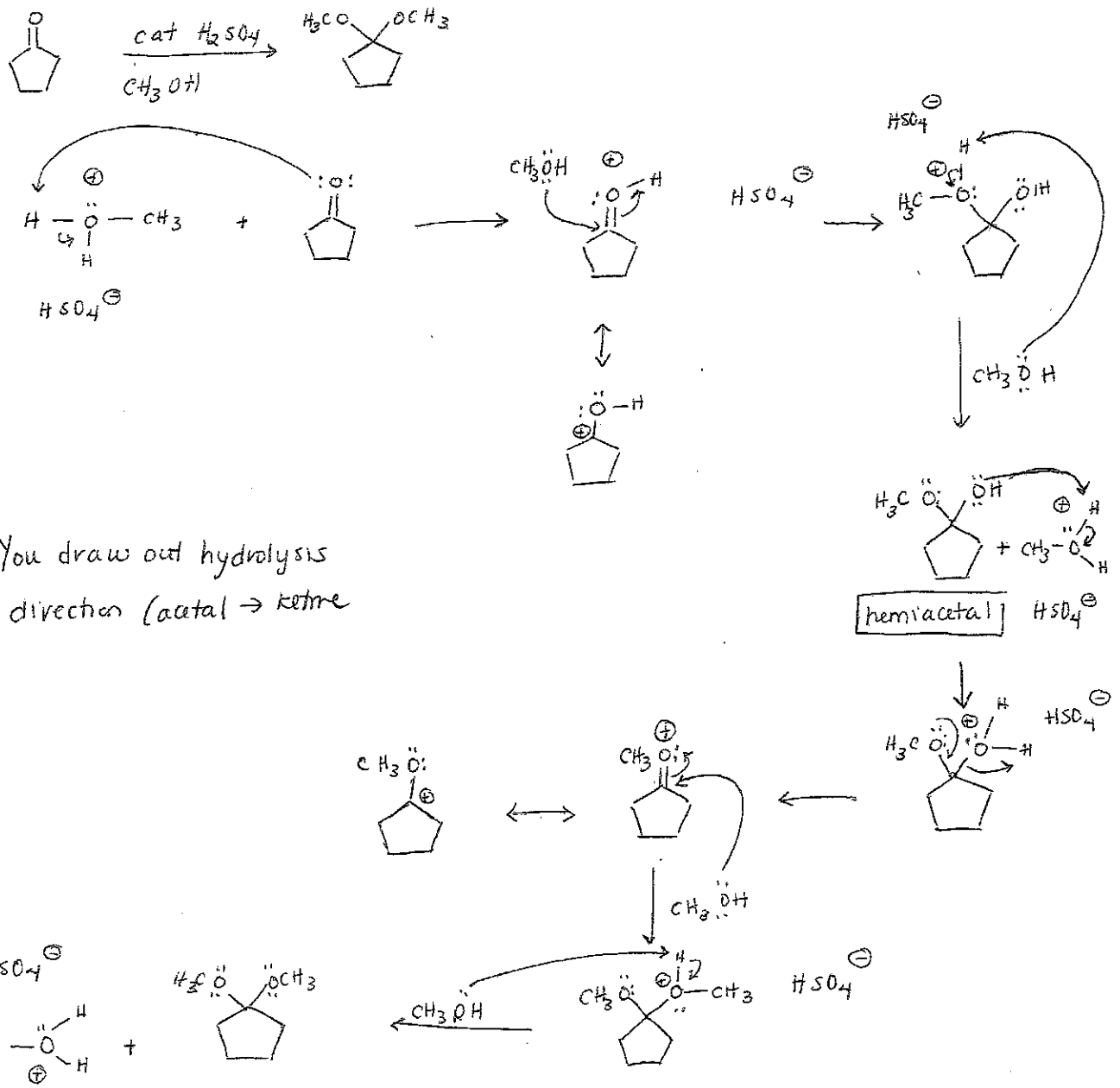
Mechanism of acetal formation:



* You draw out hydrolysis direction (acetal → ketone

* under these conditions hemiacetal cannot be isolated